

Design and Synthesis of Three-Dimensional Organic Structures

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Education

2005 B.S. The University of Tokyo
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Professional Employment

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2013 Group Leader and Project Coordinator, JST ERATO Itami Molecular Nanocarbon Project (until 2020)
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Award

2013 RSC PCCP Prize
2014 Akasaki Award
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Aromatic compounds are potentially useful as functional electronic materials. However, the controlled synthesis and assembly of three-dimensional complex molecules are still very difficult, especially for the crystal engineering of organic molecules. This group aims to create novel topological and reticular organic structures by using synthetic organic chemistry and geometric insights.

To achieve our purpose, this group will start electron-diffraction crystallography (MicroED) for the rapid structure determination of organic compounds. While X-ray crystallography is a general and reliable method for structure determination, it requires ~ 0.1 mm single crystals and making such crystal sometimes needs tremendous times and efforts. Since electron beam have much higher diffraction intensity than X-ray, structural analysis can be performed even with ultra-small crystals (1 μm or less). There are many fields such as covalent organic crystals with a three-dimensional structure

and molecules with complex molecular topologies, where structural analysis has not been sufficiently developed.

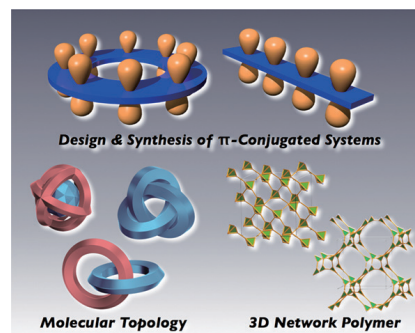


Figure 1. Design and synthesis of π -conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

Selected Publications

- Y. Saito, K. Yamanoue, Y. Segawa and K. Itami, "Selective Transformation of Strychnine and 1,2-Disubstituted Benzenes by C-H Borylation," *Chem* **6**, 985–993 (2020).
- Y. Segawa, D. R. Levine and K. Itami, "Topologically Unique Molecular Nanocarbons," *Acc. Chem. Res.* **52**, 2760–2767 (2019).
- Y. Segawa, M. Kuwayama, Y. Hijikata, M. Fushimi, T. Nishihara, J. Pirillo, J. Shirasaki, N. Kubota and K. Itami, "Topological Molecular Nanocarbons: All-Benzene Catenane and Trefoil Knot," *Science* **365**, 272–276 (2019).
- G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi and K. Itami, "Synthesis of a Carbon Nanobelt," *Science* **356**, 172–175 (2017).
- T. Yoshidomi, T. Fukushima, K. Itami and Y. Segawa, "Synthesis, Structure, and Electrochemical Property of a Bimetallic Bis-2-Pyridylidene Palladium Acetate Complex," *Chem. Lett.* **46**, 587–590 (2017).
- Y. Segawa and D. W. Stephan, "Metal-Free Hydrogenation Catalysis of Polycyclic Aromatic Hydrocarbons," *Chem. Commun.* **48**, 11963–11965 (2012).
- Y. Segawa, M. Yamashita and K. Nozaki, "Boryllithium: Isolation, Characterization, and Reactivity as a Boryl Anion," *Science* **314**, 113–115 (2006).

1. Synthesis and Reactivity of Highly Strained Belt-Shaped Polycyclic Aromatic Hydrocarbons

We performed the synthesis of novel π -conjugated molecules with high strain energies and the investigation of its structural properties.^{2–4)}

The synthesis of cyclo[pterycene] derivatives was achieved in each one step from (6,6)carbon nanobelt (Figure 2).³⁾ It was revealed that the carbon nanobelt was reacted as a diene in the Diels–Alder reaction with arynes and alkynes. Structures of all products were identified by X-ray crystallography to confirm that the Diels–Alder reactions took place at the six central benzene rings of the carbon nanobelt. DFT calculations indicated that the release of strain energy is the driving force to proceed the Diels–Alder reaction. By using this method, we have successfully synthesized cyclotetracosipterycene, the largest iptycene ever synthesized.

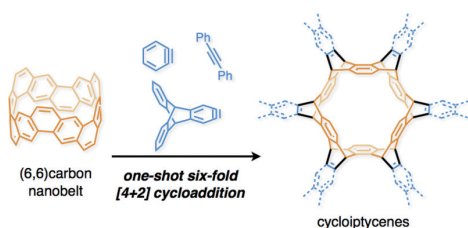


Figure 2. Diels–Alder reaction of (6,6)carbon nanobelt with alkynes and arynes for the formation of cyclo[pterycene] derivatives.

The synthesis, structure, and properties of methylene-bridged [6]cycloparaphenylene ([6]CPP), a nonalternant aromatic belt, were investigated (Figure 3).²⁾ This belt-shaped methylene-bridged [6]CPP, in which each phenylene unit is tethered to its neighbors by methylene bridges, was constructed through 6-fold intramolecular nickel-mediated aryl–aryl coupling of triflate-functionalized pillar[6]arene in 18% isolated yield. As compared to the analogous [6]CPP, the methylene bridges coplanarize neighboring paraphenylene units and enhance the degree of π -conjugation, which results in a significant decrease in energy gap. Moreover, the incorporation of small molecules in the defined pocket of methylene-bridged [6]CPP makes it an attractive supramolecular architecture. Methylene-bridged [6]CPP is characterized by high internal strain energy reaching 110.2 kcal mol⁻¹, attributed to its restricted structure. This work not only exhibits an efficient

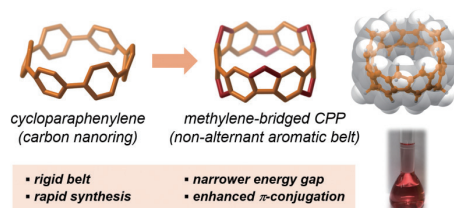


Figure 3. Synthesis of a nonalternant aromatic belt.

strategy to construct a new family of aromatic belt, but also showcases their properties, which combine the merits of CPPs and pillararenes.

2. Development of a Direct Octagon-Forming Annulation Reaction by Palladium Catalyst

The discoveries of new forms of carbon have always opened doors to new science and technology. In 1991, three-dimensional (3D) periodic carbon crystals with negative Gaussian curvatures that consist of six- and eight-membered rings were proposed. To realize these 3D periodic carbon crystals, methods for creating polyaromatic structures embedding eight-membered rings must be developed. Here the two annulative coupling reactions that form an eight-membered ring through catalytic C–H functionalization are reported (Figure 4).¹⁾ Bay-chlorinated polyaromatics undergo either annulative dimerization or cross-coupling with biphenylene in the presence of a palladium catalyst to form various hitherto inaccessible polyaromatics embedding an eight-membered ring. The threefold annulative cross-coupling of 1,5,9-trichlorotriphenylene allowed construction of a highly curved nanocarbon. The present work not only demonstrates the potential of annulative coupling for constructing octagonal nanocarbons but also provides a conceptual pathway for the synthetic realization of 3D periodic carbon crystals.

Based on this result, our group has started the Joint Research Program in IMS with Murakami group. Our group will support the rapid structural determination of targeted π -conjugated molecules, their synthetic intermediates, as well as active species of transition metal catalysts.

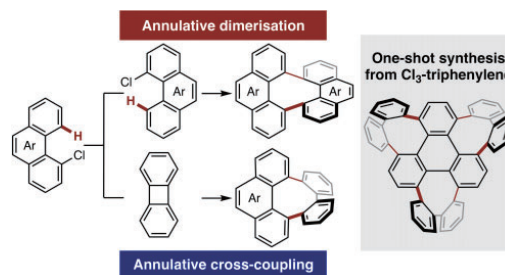


Figure 4. Palladium-catalyzed octagon-forming annulation reaction.

References

- 1) S. Matsubara, Y. Koga, Y. Segawa, K. Murakami and K. Itami, *Nat. Catal.* **3**, 710–718 (2020). doi: 10.1038/s41929-020-0487-0
- 2) Y. Li, Y. Segawa, A. Yagi and K. Itami, *J. Am. Chem. Soc.* **142**, 12850–12856 (2020).
- 3) H. Shudo, M. Kuwayama, Y. Segawa and K. Itami, *Chem. Sci.* **11**, 6775–6779 (2020).
- 4) K. Y. Cheung, Y. Segawa and K. Itami, *Chem. –Eur. J.* **26** (2020). doi: 10.1002/chem.202002316

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